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13. ABSTRACT (Maximum 200 words) A solid state NMR investigation is undertaken to characterize at the molecular level the structure and dynamic nature of epoxy resin systems cured in the presence of an active surface intended to represent an adherend surface. Comparison is made with the cure reaction in the bulk phase in the absence of a surface. This comparison focuses both on the different products and different kinetics which result from the presence of an active surface. The major system considered is that based on the diglycidyl ether of bisphenol A cured with primary amines, in particular 4,4' diaminodiphenyl sulfone. Aluminum oxide is used as a high surface area model of aluminum adherend surfaces. The NMR experiments utilize line narrowing techniques to yield resolved spectra of the solid materials. ¹³ C and ¹⁵ N NMR are used to identify the structures, with various relaxation experiments being employed to aid in the assignments and to characterize the mobility of the cured resin. This represents a new and powerful probe of surface adhesion and the understanding achieved can hopefully yield benefit in terms of improved understanding of adhesive joint performance.					
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ADHERENT SURFACE EFFECTS ON EPOXY CURE BY NMR.

FINAL TECHNICAL REPORT

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May 11, 1994.

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1. Statement of the problem.

The nature of the epoxy cure process and its practical significance in the overall problem of adhesion(1-3) is of considerable interest. In particular, a detailed molecular level understanding of the effect of varying surfaces on the adhesive cure chemistry is poorly understood, though the potential significance in terms of service life and inherent strength in an adhesive joint is great. There has been a series of investigations of the effect of various surfaces utilizing x ray, electron microscopy, DSC and Infra-red spectroscopy among other techniques (4-7). There are significant effects due to the adherend surface clearly observed, though the results are often contradictory and lack a precise molecular viewpoint. Often the surface is observed to have a catalytic effect on the cure reaction. It has also been noted that the cross-link density at the surface is changed from that of the bulk with both higher and lower cross-link density being observed depending on the system under study. The significance of higher cross-link density leading to brittle failure and lower density to poor bond properties is of obvious practical importance.

NMR can play a role in the structural elucidation of cured epoxy resins. Due to the highly cross-linked rigid product the power of the CPMAS (cross polarization magic angle spinning)(8) technique which yields high resolution spectra with resolved chemical shifts in solid samples provides one of the few legitimate structural analytical probes of these materials. The problem of very limited solubility and the structural degradation that can accompany dissolution is avoided. Thus solid state NMR techniques offer a powerful probe for the structure elucidation of these materials. CPMAS of both ^{13}C and ^{15}N can be used successfully in this regard.

Recent discussion of the theory of cure by Matsuoka et al.(9) suggest that the relaxation of the cross-linked product is of importance in determining both the rate of cure and the viscoelastic and thermomechanical properties of the resin. This is a consequence of the fact that the highly cross-linked network produced leads to a decrease in chain mobility with time thus inhibiting the cure reaction. It is desirable to not only monitor the detailed product formation but also to be able to simultaneously characterize the inherent chain dynamics in the network as the cure proceeds. Solid state NMR offers this potential and has not been applied to surface bonded resins to a significant extent.

It is the purpose of this study to apply NMR experiments to systems(10) which have been developed and characterized by Zukas et al. at the U.S. Army Materials Technology Laboratory, Watertown, Ma. These systems involve bisphenol A type epoxies and amine curing agents with particulate aluminum oxides. Studies and characterizations were made using DSC, HPLC, TGA, Mass

spectrometry and FT Raman. The results of these studies show that significantly faster reactions leading to lower Tg materials occur for activated aluminum oxide filled samples relative to unfilled samples. Further there are indications of increased rates of amine addition and the occurrence of epoxy homopolymerization not present in unfilled samples. Homopolymerization and strong epoxy/surface interactions clearly distinguish this behaviour from the traditional bulk amine/epoxy cure. The precise nature and structure of the "interphase" region however is uncertain and an understanding of this is critical in terms of defining adhesive/adherend interactions. The presence of water, arising from the cure reaction itself or added, is known to have a significant role in the nature of the end product and its eventual degradation. This active ingredient exhibits different effects in the filled and unfilled cases, a consequence, at least in part of the influence of surface-water interactions. A detailed understanding of the chemistry at the molecular level in these systems together with the existing characterizations(10) will provide a basis for discussing the factors involved in determining adhesive joint performance. It is the purpose of this work to apply a series of NMR experiments to the resolution of some of these questions.

2. Summary of results.

The structure and dynamics of the cure of the epoxy resin system based on the diglycidyl ether of bisphenol-A (DGEBA) is investigated using primarily solid state NMR techniques. The curing agent is a typical primary amine: 4,4'-diaminodiphenyl sulfone (DDS) and the purpose of the study is to contrast the behaviour of the cure in the presence and absence of an active surface. In this study finely divided basic activated aluminum oxide is used as a high surface area model for aluminum adherend surfaces.

An experimental protocol which allows the spectroscopic examination of samples at different extents of cure will be established. Quenching at different degrees of cure and maintaining a stable structure over the time period required for NMR investigation is necessary in this regard.

NMR line narrowing techniques using magic angle spinning (MAS) in combination with cross polarization (CP) can yield analytic spectra of the cured resin giving detail on the extent of cure and the structure. Both ^{13}C and ^{15}N can be used as probe nuclei to focus on the epoxy opening and crosslink detail.

(a) Experimental.

A sample of an exactly known weight of an epoxy resin (DGEBA), obtained from Dow Chemical Co. (der 332) was heated in the oven at temperature 160°C until completely melted. The sample was cooled and at the room temperature appropriate amounts of curing agent (DDS) at the stoichiometric ratio were added and mixed for a short period of time. The resin formulation was next pre-heated in the oven to 160°C for 1.5 min. to completely dissolve the curing agent in the epoxy resin and immediately cooled on dry ice to quench the cure reaction. At low temperature, alumina was added to the resin mixture at an equal weight to weight of the resin formulation. The sample was chilled to the temperature of liquid nitrogen and cryogenically milled by using a SPEX Freezer/Mill for 6 min. to achieve the necessary degree of particle size and uniformity. In a closed aluminum container, a small amount of mixture was isothermally cured in the oven for preset time. Immediately after, the sample was cooled on dry ice and finely milled in the SPEX Freezer/Mill for 3 min under the same cryogenic conditions as previously.

It is assumed that the degree of cure is negligible during the 1.5 min. dissolving period for the sample in the absence of activated aluminum oxide. DSC at 140°C (10), for the stoichiometric resin mixture shows the correctness of this assumption. In this way uniformity of distribution of a curing agent in an epoxy resin is obtained.

The solid CPMAS ^{13}C spectra (74.6Mhz) were recorded with a contact time 5ms and an interval of 5s between pulse sequences at temperatures in the range of 250K to 300K on a Bruker MSL300 NMR spectrometer. Spinning rates of approximately 5kHz were used and an average of 512 contacts was necessary.

Fourier transform infrared spectra were also recorded with Perkin Elmer 1600 FT spectrometer to compare the epoxy to ether conversion with the NMR analysis.

(b) Results and Interpretation.

The mixture of DGEBA with DDS was studied at temperature 160°C. The opening of the DGEBA epoxy ring was evidenced by the intensity of the carbon resonance at 50.7 ppm, the other peaks remaining relatively unaffected as shown below on the typical spectra. The ^{13}C CPMAS spectra: A and B were obtained for the uncatalyzed system at a cure times of 20 min. and 45 min. respectively. An internal intensity standard was available from resonances which are unaffected by the curing reaction, in this case the peak at 31.2 ppm which corresponds to $^{-13}\text{CH}_3$ of the isopropylidene group was chosen as a reference standard.

The rate of disappearance of the epoxy moiety during cure at temp.160°C is shown in Fig1.

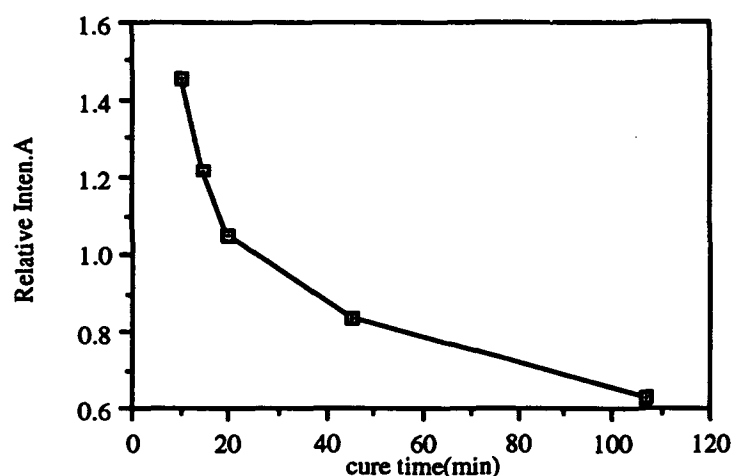
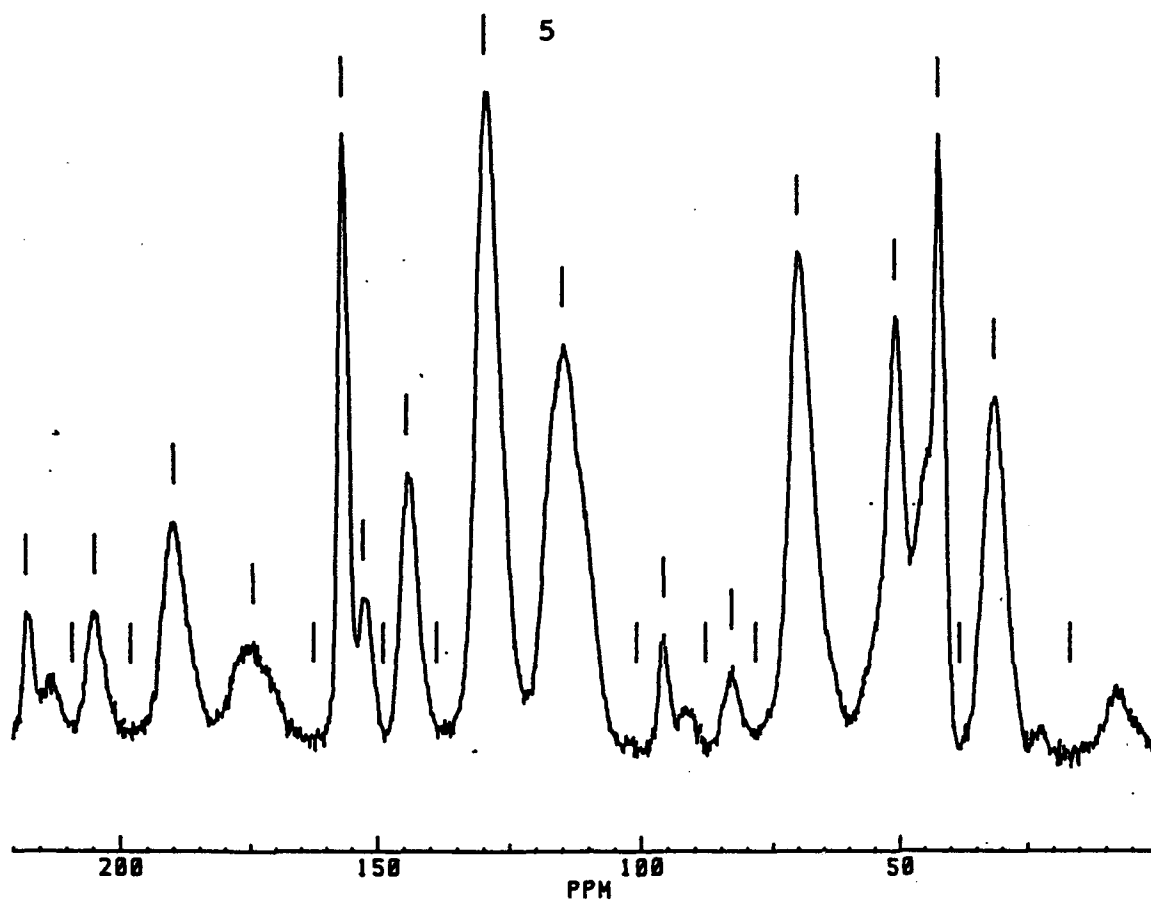


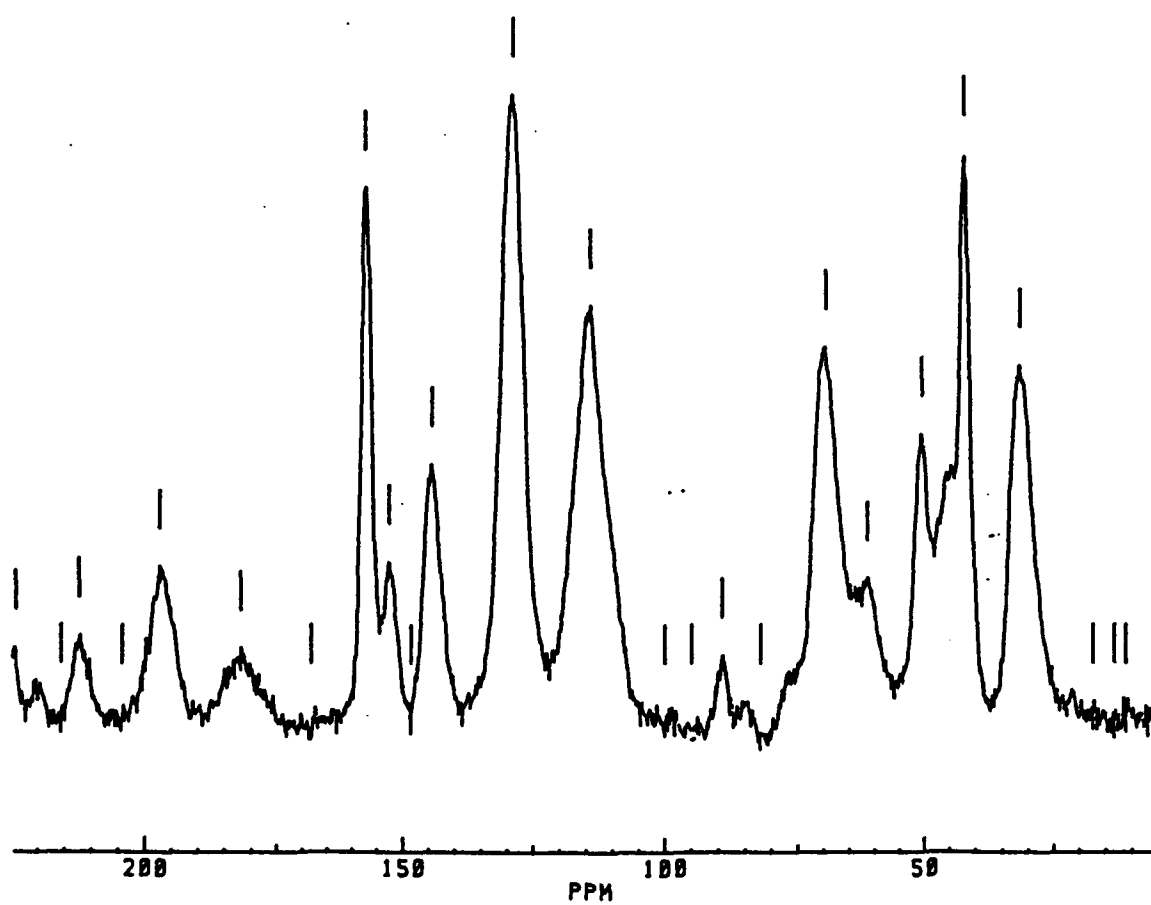
Fig1. Disappearance of the epoxy resonance in DGEBA/DDS.

Assuming first order kinetics in the short time regime (0-20min.) the

(A)



(B)



psuedo first order rate constant can be evaluated as 0.033 min^{-1} in good agreement with other estimates(10,11). The non linear character of epoxy decay implies a complex cure mechanism. Similarly the dependence of $1/\text{concentration}$ versus time for classic second order kinetics is also non linear, again indicative of a complex mechanism as has been suggested by other investigators(11,12).

In a similar manner the the reaction between DGEBA and DDS in the presence of basic aluminum oxide was analyzed in the temperature range 110-140°C and for the cure times in the range 30-120 min. The rate of disappearance of the epoxy group during the curing of the resin with basic activated aluminum oxide at various temperatures is shown in Fig 2.

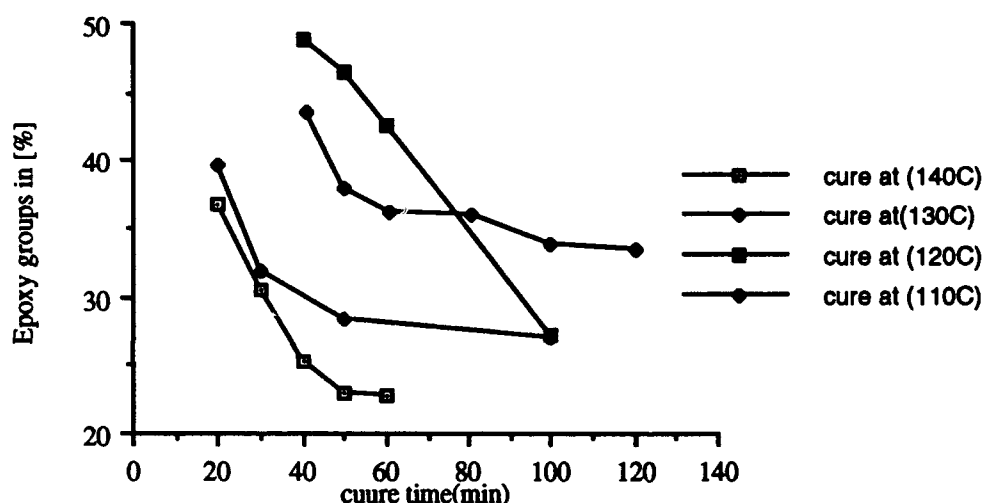


Fig.2 The influence of alumina on the DGEBA/DDS reaction rate.

A direct comparison between the presence and absence of the alumina surface can be seen in Fig.3 where the data at a temperature of 160°C for system in the absence of alumina is compared with the data in the presence of alumina at 110°C. This clearly demonstrates the magnitude of the catalytic effect in terms of a 50° temperature shift to produce the same extent of reaction.

From the data it is clear that for the uncatalized system at a cure temperature of 160°C and the curing time of 104 min. there is still about 30% of unreacted epoxy groups. This reflects the inhibition of the cure caused by decreased mobility and densification of the resin as the crosslinking increases. This effect is diminished, however, as the cure temperature increases, as can

be seen in the alumina containing (filled) samples.

It is also observed that the linewidths for the filled samples are consistently less than those for the resins prepared without the presence of alumina. The typical values being 300Hz for the filled sample and 400Hz for the unfilled case. This implies more inherent mobility in the case of the resin prepared in the presence of catalyst. This is in agreement with the DSC measurements of Zukas et al.(10) in which lower T_g materials were observed in this case. The implication of this in terms of resin structure is that a lower crosslink density results in cure in the presence of surface. This can be verified using ^{15}N NMR to probe the crosslinks involving DDS as indicated below.

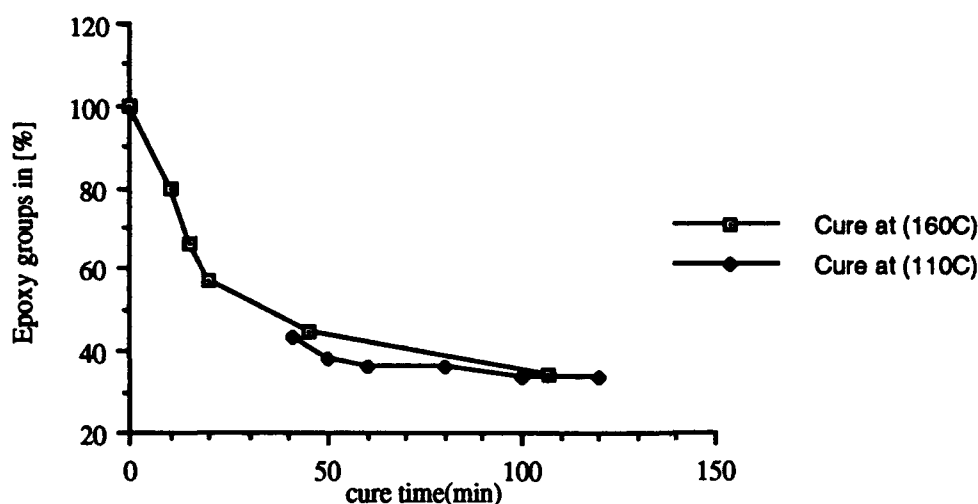


Fig3. Cure in the presence (110°C) and absence (160°C) of alumina.

Fourier Transform infra-red spectroscopy shows similar trends to the CPMAS results but quantification is more difficult. However it does appear that FTIR allows one to conveniently follow the cure qualitatively. In this case the band at 1508 cm^{-1} corresponding to the phenyl groups can be used as an internal reference standard while the decreasing epoxy band at 908.1 cm^{-1} and the increasing ether bands at ca. 1100 cm^{-1} monitor the reaction extent.

The complete elucidation of the structure of the cured resin requires the analysis of the crosslinks and the functionality distribution of the amine links. This can be addressed using ^{15}N NMR, again in the CPMAS experiment. In this regard DDS with ^{15}N isotopic enrichment of the amino groups has been obtained

by custom synthesis from "Isotec" to be used to produce the cured resin using the same protocol as before.

This grant was originally proposed as a three year project to ARO but due to lack of funds was unfunded in the third year. We intend to complete the research as outlined, however, using the materials in hand (eg ^{15}N labeled DDS), the NMR facilities at Clark and with the collaboration of Walter Zukas, US Army Materials Technology Laboratory. Subsequent publications will be forwarded on completion.

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 Yong Zhu, Research assistant
 Michael T. Hansen, Research associate

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